

OPTICALLY TRANSPARENT NANOPOROUS GLASS-POLYMER COMPOSITES

D. J. O'Brien, T. F. Juliano, P. J. Patel and S. H. McKnight

U.S. Army Research Laboratory, Weapons and Materials Research Directorate
Aberdeen Proving Ground, MD 21005

ABSTRACT

Proper design of lightweight laminated composite armor relies on the engineer's ability to specify the acoustic impedance of each layer. In conventional, opaque laminated armor systems, stress waves can be efficiently transmitted throughout the structure with a gradual variation of the acoustic impedance from one layer to the next. In transparent systems, however, the engineer can only choose between monolithic glass, ceramic, or polymer systems, resulting in a large acoustic impedance "jump" between polymer and ceramic layers. In this work we manufacture a novel transparent polymer-glass composite to be used as an intermediate impedance material. This transparent nanocomposite is created by infiltrating nanoporous glass (Vycor, Corning Inc.) with different polymers. The Vycor pores (4-6 nm) are much smaller than the wavelength of light, thus refractive index matching with the polymer is not necessary for transparency.

1. INTRODUCTION

In order to field a more agile, survivable, and mobile fighting force, the Army is facing critical needs for lightweight, transparent armor material systems. Presently, to satisfy performance requirements, minimize weight, and maintain transparency these systems consist of a laminated stack of materials with widely varying mechanical properties, Figure 1. Each material is selected for specific functions and must also work as part of the system to defeat a given threat. In order for the laminate to work efficiently, stress waves must be transferred from one layer to the next (Li, 2001; Tasdemirci and Hall, 2005). When the stress wave crosses a dissimilar materials interface a portion of the wave is reflected. The intensity of the reflection increases with the difference in the materials' acoustic impedances, Z ,

$$Z = \rho \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}} \quad (1)$$

where ρ , E , and ν are the density, Young's modulus, and Poisson's ratio, respectively.



Figure 1: Schematic of simple transparent laminate

The shock-wave mitigation of laminated structures can be significantly improved through the gradual variation of Z through the structure's thickness. For systems that do not require transparency, polymer composites are a natural choice for such "intermediate Z " materials since matrix and reinforcement type as well as relative volume fraction may be chosen to engineer a wide range of impedance values. Unfortunately, composite materials are not typically transparent. In order to maintain transparency in traditional composites, constituent refractive indices must be precisely matched to better than one part in one thousand. Furthermore, due to the temperature dependence of the matrix refractive index, the composite is transparent over a relatively narrow temperature range. Newly developed clay- or nanofiber-based polymer nanocomposites are often transparent since the characteristic size of the reinforcement is much less than the wavelength of incident light. However the volume fraction of reinforcement in these systems is very low and does not provide a significant increase in impedance over neat polymers. As such, a transparent intermediate impedance material does not presently exist. Micromechanical predictions suggest that an interpenetrating network of nanoporous glass and polymer should produce such a material if it can be fabricated. In this work, a novel transparent "intermediate Z " material is developed by infiltrating nanoporous Vycor glass (Corning Inc.) with appropriate polymers.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 NOV 2006		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Optically Transparent Nanoporous Glasspolymer Composites				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory, Weapons and Materials Research Directorate Aberdeen Proving Ground, MD 21005				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM002075., The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Vycor is nanoporous glass manufactured by Corning, Inc. from a soft alkali-borosilicate glass. Upon annealing at moderate temperature, the glass phase separates into two interpenetrating phases one of which is rich in alkali and boric oxide. This phase is slowly leached away in a hot dilute acid bath leaving behind a porous glass of approximately 96% silica (Elmer, 1992). The process results in pores (4-6 nm) that are much smaller than the wavelength of light, thus refractive index matching with the polymer is not necessary to produce transparent composites (Krauthausen et al., 2005).

There is a considerable amount of literature on nanoporous glass such as Vycor. Typically researchers use the material to study fundamental polymer thermodynamic transitions in confined spaces (for example: Crupi et al., 2005; Tombari et al., 2005; Swenson, 2004; Lal et al., 1997; Zarbin et al., 1997). Lal *et al.* studied the behavior of polystyrene chains in solution while confined inside nanoporous glass; Zarbin *et al.* produced Vycor-polyaniline nanocomposites; and Mirau and Hefner infused Vycor with polyethyl acrylate for nuclear magnetic resonance studies of the polymer confined in the pores. Vycor has also been used as a template material. Giunta *et al.* (2005) infused Vycor with polyacrylonitrile in order to convert the glass-polymer composite to a carbon-silica composite through pyrolysis. Sotomayor *et al.* (2001) used polyaniline-infused Vycor to produce a pH sensor, and Schnoes (1999) used polymer-filled Vycor as a holographic recording medium.

Although some authors have considered the infiltration of Vycor with polymers, most of the studies to date have not considered the mechanical behavior of such a material. Abramhoff and Klein studied the mechanical behavior of microporous glass-PMMA composites (Abramhoff and Klein, 1990). Liu performed an extensive study on the processing and properties of Vycor glass and found that with careful manufacturing the material is transparent (Liu, 1980). His study included characterization of the material's properties including density, stiffness, strength, and thermal expansion coefficient, among others. Several years later, this effort was extended with a study on the mechanical properties of PMMA-impregnated porous glasses over a range of volume fractions (Pope et al., 1989).

In this work we will explore the processing and mechanical behavior of infused Vycor along with its optical properties to assess its viability as a component of a transparent armor laminate. A variety of characterization techniques, both at the micro and macro-scale, are used to evaluate the Vycor-polymer composite

2. EXPERIMENTAL PROCEDURE

2.1 Processing

Three different monomers were considered for infiltration of the Vycor 7930 glass (Corning, Corning, NY) with 4-6 nm diameter pores; low viscosity Spurr epoxy (Polysciences, Inc., Warrington, PA), isobornyl acrylate (IBA) (Sigma-Aldrich, St. Louis, MO) and methyl methacrylate 99% (MMA) (Sigma-Aldrich). Viscosity at room temperature for the Spurr epoxy is 60 cP, for IBA, 2.6 cP and for MMA, 0.6 cP. Both the IBA and MMA monomers contained small amounts (10-200 ppm) of inhibitor (4-methoxyphenol, MEHQ) that was removed via an extraction process that was necessary to prevent material discolorations. The extraction process consisted of mixing the monomer once in a separation funnel with a 1% by weight NaOH solution (0.37M), followed by two rinses of deionized water, and concluded with a single rinse of brine solution to remove any water from the mixture. The Spurr epoxy was used as received.

Various geometry Vycor pieces of thicknesses roughly 3 and 6 mm were cleaned of any contamination though high temperature treatment in a programmable temperature controlled oven. Samples were first heated at a rate of 1 °C/min from room temperature to 80 °C, and held for two hours to allow organic contaminants and any moisture to evaporate out. Next, the samples were heated to 600 °C at a rate of 1 °C/min, and this temperature was held for at least 24 hours before gradual cooling. Higher heating rates often resulted in catastrophic failure of the material through numerous internal cracks, perhaps due to nonuniform heating of the specimen or as contaminants inside the pores boiled. Certain Vycor specimens were treated with a silane coupling agent (3-methacryloxypropyltrimethoxy silane, MPS) to improve bonding between the monomer and the Vycor. The silane solution was 1% MPS by weight in an ethanol/water solution (90/10, w/w) with pH adjusted to 4.5 using acetic acid. After stirring the solution for one hour, the Vycor was soaked for 30 minutes. Finally, the sample was removed from solution and held at 95 °C for 1 hr to condense and crosslink the silane on the surface of the glass. Vycor pieces were kept in a nitrogen environment shortly after the cleaning process.

Infiltration and curing procedures varied for each of the pre-polymers. Samples soaked in Spurr epoxy at ambient conditions were allotted three days before curing the resulting pieces at 70 °C for 12 hr. Samples infiltrated with IBA and MMA were cured either with ultraviolet light or at temperatures near 60 °C for at least 12 hr. Benzyl peroxide (BP) was used as a thermal initiator for both the IBA and MMA filled samples.

The IBA processing schedule was as follows. First, either 0.5% or 1.0% by weight BP was dissolved into IBA. Next, to prevent oxygen inhibition of the free radical polymerization, the resulting solution was bubbled with nitrogen gas in a vial for at least 20 minutes to remove any oxygen. A Vycor piece was placed in the vial, which was capped off to exclude any oxygen reentry. The samples soaked at room temperature for 24 hr, and then placed in fresh nitrogen-bubbled IBA solution without initiator at 40 °C for 3 days. This ensures there is a suitable initiator concentration gradient in the material, with the initiator assisting to polymerize the sample from the inside first. In this way, as the material shrinks during polymerization, new monomer is available from the surrounding solution. Finally, the samples were removed from solution and allowed to cure at 60 °C for 3 days.

The final MMA infiltration processing schedule consisted of the following steps. First, 1.5% by weight BP was dissolved into the MMA and purged with nitrogen as before. The Vycor piece was placed into solution for about 30 minutes, which is enough time for MMA to completely saturate the pores (Liu, 1980). Next, the sample was placed in a nitrogen-bubbled 0.25% BP solution of MMA and polymerized in a convection oven for 3 days at 32 °C. As with the IBA sample, the specimen was transferred to a new polymer solution with reduced initiator concentration in to promote polymerization from the “inside-out.” Finally, the samples were cured at 60 °C for 12 hr. After polymerization, excess PMMA was removed by cutting and grinding. To facilitate post processing, Vycor pieces were placed between Teflon sheets for easier removal of excess PMMA. Before this final processing schedule, many different polymerization times and BP concentrations (from 0.05% to 3%) were attempted, however, results were not optimal.

2.2 Physical Property Characterization

To determine if the polymerization of MMA was affected by the nanoporous environment, the molecular weight of material polymerized inside the pores was compared to that polymerized of the bulk under the same conditions. In order to remove the PMMA from the pores, a 370 mg piece of infiltrated Vycor was submerged in 4 mL tetrahydrofuran (THF) overnight. After soaking the Vycor, it was dried at 90 °C for 6 hours and weighed to estimate the mass of PMMA leached out of the system. A small sample of PMMA that polymerized external to the Vycor was taken and dissolved in THF. The molecular weight of the samples was determined with gel permeation chromatography (GPC). As a comparison, a standard sample with a known molecular weight of 540 kD (Scientific Polymer Products) was also tested.

The density of the specimen was measured using Archimedes principle and the extent of pore filling was estimated using the rule of mixtures. The density of the glass phase was taken as 2.18 g/cm³, assuming the density of PMMA is 1.15 g/cm³, and the internal pore volume in the Vycor is 28% (Elmer, 1992). The optical quality (transmission, haze, clarity) was assessed with a haze meter (Haz-gard plus, Byk-Gardner, Columbia, MD).

Atomic force microscopy (AFM) was used to gather topographical information on cleaved surfaces of borosilicate Starphire glass, unfilled Vycor, and PMMA-filled Vycor (see Table 1). Images were obtained in tapping mode on a Digital Instruments Dimension 3100 Atomic Force Microscope (Veeco Metrology, Santa Barbara, CA).

2.3 Mechanical Property Characterization

Depth-sensing indentation was performed on Vycor specimens with a Nano Indenter XP (MTS Nano Instruments, Knoxville, TN). A total of 75 5- μ m-deep indentations were made on three different Vycor samples, each polished to a 1 μ m finish. One sample was unfilled and the other two were filled with one treated with silane. A cube corner indenter geometry was used to promote cracking around the impressions. Indentation strain rate was 0.1 s⁻¹ for all tests.

The tensile modulus of the filled specimens (20x3.4x1.7 mm) was measured under three-point bending using a dynamic mechanical analyzer, (TA Instruments, New Castle, DE). The mechanical properties were also measured using ultrasonic wave speed. Specimens 3.5 mm thick were manufactured as described above. Pulser-receiver transducers (Panametrics-NDT, Waltham, Massachusetts) were used to measure the longitudinal (transducer model V111, 10 kHz) and shear (transducer model V155, 5 kHz) wave speeds. The transducers were placed on the sample with a thin layer of honey to act as a coupling agent. The shear (G) and tensile (E) moduli were then calculated with,

$$G = \rho v_s^2 \quad (2)$$

$$E = \rho v_s^2 \frac{\left(3 \left(\frac{v_l}{v_s} \right)^2 - 4 \right)}{\left(\frac{v_l}{v_s} \right)^2 - 1} \quad (3)$$

where ρ is the density and v_s and v_l are the shear and longitudinal wave speeds, respectively.

The modulus of rupture (MOR) was used to characterize the strength of the filled material according

to ASTM C158-02. A 100x100x3.2 mm thick plate was infiltrated with PMMA as described, and a surface grinder (FSG-3A1020, Chevalier Machinery, Santa Fe Springs, CA) was used to cut the plate into beams nominally 100x10x3.2 mm. After cutting, the beams were polished with progressively finer grit silicon carbide papers down to a final grit with a 6.5 μm average particle size. The specimens were observed with a polarimeter (PS100, Strainoptics, North Wales, PA) to assess the residual stress state. The MOR tests were conducted in four point bending on a load frame (Synergie, MTS Systems, Eden Prairie, MN) fitted with a 500 N load cell. As shown in Figure 2, the top and bottom spans were 55 mm and 85 mm, respectively. Eight samples were tested to failure at a constant displacement rate of 0.2 mm/min, and the MOR was calculated according to the ASTM standard with the beam equation for four point bending:

$$MOR = \frac{3Pa}{bd^2} \quad (4)$$

where P is the maximum load, a is the length of the moment arm span, b is the width of the specimen, and d is the thickness.

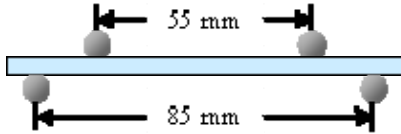


Figure 2: Schematic of MOR experiment.

3. RESULTS AND DISCUSSION

The feasibility of manufacturing a nanocomposite from nanoporous glass was first tested by infiltrating Vycor glass with various prepolymers (methyl methacrylate (MMA), isobornyl acrylate (IBA), and a low viscosity epoxy) after thorough glass cleaning and surface modification procedures.

Table 1 shows the density of the various specimens as well as the estimates for the fraction of pores filled. We found that the epoxy used was too viscous to properly infiltrate the glass. The IBA filled the pores reasonably well, but resulted in specimens with a slightly yellowish tint and were difficult to process after curing. The MMA filled the pores better than the other polymers and resulted in a clear, colorless material with 88.5% transmission, 7.9 % haze, and 97.7% clarity.

Our most successful results occurred with MMA. These experiments showed that the nanoporous glass can be easily filled with the low viscosity monomer at ambient conditions, as has been previously illustrated

(Liu, 1980). The MMA will saturate the nanoporous network in a few minutes by simply soaking the glass in the monomer. Optical clarity is maintained when polymerization proceeds slowly in excess monomer to allow diffusion of the monomer in the porous glass to offset shrinkage induced voids within the sample. The process produces specimens with excellent optical quality (Figure 3), near 100% pore filling with polymers possessing molecular weight similar to bulk polymerization.

Table 1: Density and fraction of pore volume filled for various polymer-Vycor composites. Methyl methacrylate (MMA), Isobornyl acrylate (IBA), epoxy (Spurr® epoxy)

Polymer	Composite density (g/cm ³)	Fraction pore filled
MMA	1.85	0.87
IBA	1.80	0.73
epoxy	1.63	0.19



Figure 3: PMMA-filled Vycor specimens: (top) polymerized quickly outside of solution (bottom) polymerized slowly in solutions of decreasing initiator concentration.

Through stress-induced birefringence, the polarimeter reveals information about the stress state of the specimen in the plane of the image. Figure 4 shows polarimeter images taken from the top and side of one of the MOR beams. In general, the image consists of two superimposed fringe patterns: isoclinic and isochromatic. The isoclinic fringes correspond to lines where the principle directions of the in-plane stress field coincide with the axis of the polarizer while isochromatics corresponds to lines of constant stress difference ($\sigma_1 - \sigma_2$). Since the 'top view' in figure 4 is uniformly dark, we can conclude that the specimen is relatively free of residual stress in the plane. The side view, conversely, does reveal a fringe pattern through the thickness of the specimen that is not symmetric. The apparent stress field in the thickness direction could be a result of non-

Table 2: Properties of various transparent materials.*

	Glass (Starphire™)	Vycor-PMMA	PMMA	Vycor (unfilled)
Density (g/cm ³)	2.50	1.81	1.2	1.45
Young's modulus (GPa)	73.1	30	6.1	17
Acoustic Impedance (kg/(m ² -s))	14.6	7.8	3.2	4.85

* From ultrasonic measurement.

uniform infiltration and polymerization of MMA through the thickness. The asymmetry could be due to how the specimen was polymerized. For example, the layer of excess PMMA was thicker on one side of the specimen than the other, which could lead to polymerization shrinkage-induced bending of the plate. Or, the polymerization rate on one side might have been faster than the other due oxygen inhibition and the increased exposure to air on one side of the specimen.

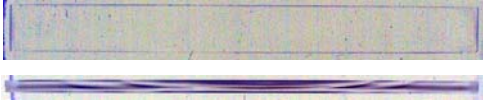


Figure 4: Polarimeter images of MOR specimens, top view (top), side view (bottom).

AFM scans revealed that the cleaved texture of both the filled and unfilled Vycor specimens (Figure 5a) were much rougher than the Starphire glass (Figure 5b). The surface of the Vycor specimens has a nodular texture with a feature size of approximately 100 nm in diameter. The rough nature of the cleaved surface could be an indication of a tortuous crack path that may result in greater energy absorption as compared to monolithic glass.

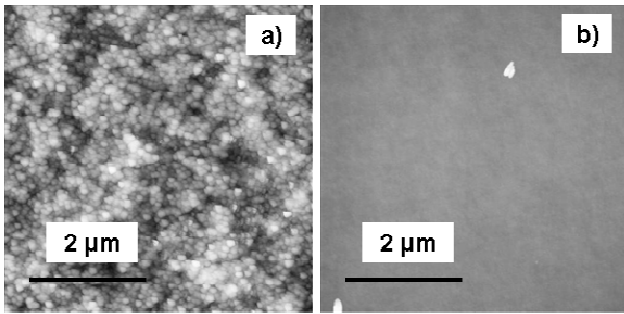


Figure 5: AFM topology scans of filled Vycor (a) and Starphire glass (b) cleaved surfaces. The height contrast scale in both images is 200 nm.

The mechanical properties of the resulting PMMA-infused materials were quantified with measurements at various length and time scales. Depth-sensing indentation showed that Young's modulus of the porous material increased from 19 GPa to 30 GPa for both the silane and non-silane treated samples. Indentation hardness of the filled samples was about 3.25 GPa compared to 2.00 GPa for the unfilled sample.

Three-point bending shows an increase in modulus from 17 GPa to 23 GPa, while ultrasonic measurements gave moduli of 15 GPa and 29 GPa for unfilled and filled specimens, respectively. These results agree well with micromechanics calculations for composites consisting of two interpenetrating networks (Nielsen and Landel, 1994; Feng et al., 2004) which predict a modulus of ~33 GPa for the of the Vycor-PMMA composite. The modulus of rupture of the PMMA-filled Vycor was 43.6 ± 4.6 MPa compared 38.8 ± 5.0 MPa for a borosilicate monolithic glass tested under similar conditions.

Most importantly, as Table 2 shows, the acoustic impedance of the nanocomposite, at $7.8 \text{ kg}/(\text{m}^2\text{-s})$, is an excellent intermediate value between that of a glass-ceramic face plate ($14.8 \text{ kg}/(\text{m}^2\text{-s})$) and a polymer backing material ($3.2 \text{ kg}/(\text{m}^2\text{-s})$).

4. CONCLUSIONS

This nanocomposite material, with an intermediate impedance, will provide transparent armor designers with access to material properties not previously available and could lead to enhanced lightweight protection for the soldier. Figure 6 is an image of such a laminate. The laminate was constructed of 9 mm thick borosilicate glass and 5 mm thick polycarbonate with a 3 mm thick Vycor-PMMA nanocomposite interlayer. Similar to the specimen shown in Figure 7, the interlayer was only rough ground to remove the excess PMMA. In order to make the specimen transparent the laminate was then bonded together using an epoxy with refractive index very close to that of the Vycor-PMMA nanocomposite. The index-matched epoxy eliminated the scattering at the two interfaces resulting in a transparent laminate (85.8% transmittance, 4.2% haze, 93.9% clarity). This process shows that such transparent laminates can be manufactured.



Figure 6: Laminate of polycarbonate and borosilicate glass (9 mm) and polycarbonate (5 mm) with Vycor-PMMA interlayer (3 mm).

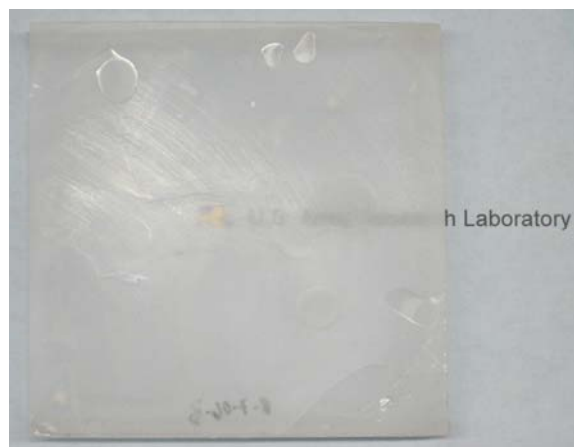


Figure 7: Vycor-PMMA composite plate after processing before incorporating into laminate using refractive index matched adhesive.

REFERENCES

- Abramhoff, B. and L. C. Klein, 1990: PMMA-Impregnated Silica Gels: Synthesis and Characterization. *Sol-Gel Optics, SPIE Vol. 1328*, 241-248.
- Crupi, V., D. Majolino, P. Migliardo, and V. Venuti, 2005: Dynamical properties of liquids in restricted geometries. *Journal of Molecular Liquids*, **117**, 165-171.
- Elmer, T. H., 1992: Porous and Reconstructed Glasses., *Engineered Materials Handbook, Vol 4, Ceramic and Glasses*, A. International, Ed., 427-432.
- Feng, X. Q., Z. Tian, Y. H. Liu, and S. W. Yu, 2004: Effective elastic and plastic properties of interpenetrating multiphase composites. *Applied Composite Materials*, **11**, 33-55.
- Giunta, P. R., L. J. van de Burgt, and A. E. Stiegman, 2005: Production and characterization of carbon-silica nanocomposites from the pyrolysis of polyacrylonitrile in a porous silica matrix. *Chemistry of Materials*, **17**, 1234-1240.
- Krauthauser, C., J. M. Deitzel, D. J. O'Brien, and J. Hrycushko, 2005: Optical Properties of Transparent Resins with Electrospun Polymer Nanofibers, in *Polymeric Nanofibers. Polymeric Nanofibers*, D. H. Reneker and H. Fong, Eds., American Chemical Society, 353-369.
- Lal, J., S. K. Sinha, and L. Auvray, 1997: Structure of polymer chains confined in Vycor. *Journal De Physique II*, **7**, 1597-1615.
- Li, Y., K. T. Ramesh, and E. S. C. Chin, 2001: Dynamic characterization of layered and graded structures under impulsive loading. *International Journal of Solids and Structures*, **38**, 6045-6061.
- Liu, C. C., 1980: The Preparation and Properties of Porous Glass-Polymer Composites, Engineering, University of California Los Angeles, 193.
- Mirau, P. A. and S. A. Heffner, 1999: Fast magic-angle proton NMR studies of polymer interfaces in poly(ethyl acrylate)/Vycor composites. *Macromolecules*, **32**, 4912-4916.
- Nielsen, L. E. and R. F. Landel, 1994: *Mechanical Properties of Polymers and Composites*. Marcel Dekker Inc.
- Pope, E. J. A., M. Asami, and J. D. Mackenzie, 1989: Transparent Silica Gel-Pmma Composites. *Journal of Materials Research*, **4**, 1018-1026.
- Schnoes, M. G., L. Dhar, M. L. Schilling, S. S. Patel, and P. Wiltzius, 1999: Photopolymer-filled nanoporous glass as a dimensionally stable holographic recording medium. *Optics Letters*, **24**, 658-660.
- Sotomayor, P. T., I. M. Raimundo, A. J. G. Zarbin, J. J. R. Rohwedder, G. O. Neto, and O. L. Alves, 2001: Construction and evaluation of an optical pH sensor based on polyaniline-porous Vycor glass nanocomposite. *Sensors and Actuators B-Chemical*, **74**, 157-162.
- Swenson, J., 2004: The glass transition and fragility of supercooled confined water. *Journal of Physics-Condensed Matter*, **16**, S5317-S5327.
- Tasdemirci, A. and I. W. Hall, 2005: Experimental and modeling studies of stress wave propagation in multilayer composite materials: Low modulus interlayer effects. *Journal of Composite Materials*, **39**, 981-1005.
- Tombari, E., G. Salvetti, C. Ferrari, and G. P. Johari, 2005: Thermodynamic functions of water and ice confined to 2 nm radius pores. *Journal of Chemical Physics*, **122**.
- Zarbin, A. J. G., M. A. dePaoli, and O. L. Alves, 1997: New polyaniline porous glass composite. *Synthetic Metals*, **84**, 107-108.